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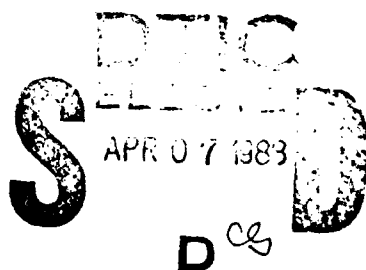
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NRL Memorandum Report 6417

FILMCAL **An ESR Simulation Program for Transition Metals in** **Phthalocyanine Films**

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Polymeric Materials Branch
Chemistry Division



February 24, 1989

SECURITY CLASSIFICATION OF THIS PAGE

ADA 206441

REPORT DOCUMENTATION PAGE				Form Approved OMB No 0704-0188	
1a REPORT SECURITY CLASSIFICATION UNCLASSIFIED			1b RESTRICTIVE MARKINGS		
2a SECURITY CLASSIFICATION AUTHORITY			3 DISTRIBUTION AVAILABILITY OF REPORT Approved for public release; distribution unlimited.		
2b DECLASSIFICATION/DOWNGRADING SCHEDULE			5 MONITORING ORGANIZATION REPORT NUMBER(S)		
4 PERFORMING ORGANIZATION REPORT NUMBER(S) NRL Memorandum Report 6417			5 MONITORING ORGANIZATION REPORT NUMBER(S)		
6a NAME OF PERFORMING ORGANIZATION Naval Research Laboratory		6b OFFICE SYMBOL (If applicable) Code 6120		7a NAME OF MONITORING ORGANIZATION	
6c ADDRESS (City, State, and ZIP Code) Washington, DC 20375-5000		7b ADDRESS (City, State, and ZIP Code)			
8a NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research		8b OFFICE SYMBOL (If applicable)		9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c ADDRESS (City, State, and ZIP Code) Arlington, VA 22217		10 SOURCE OF FUNDING NUMBERS			
		PROGRAM ELEMENT NO		PROJECT NO	TASK NO
				WORK UNIT	ACCESSION NO
11 TITLE (Include Security Classification) FILMCAL: An ESR Simulation Program for Transition Metals in Phthalocyanine Films					
12 PERSONAL AUTHOR(S) Pace, M.D. and Masumura, S.M.					
13a TYPE OF REPORT		13b TIME COVERED FROM 6/88 TO 3/88		14 DATE OF REPORT (Year, Month, Day) 1989 February 24	
				15 PAGE COUNT 29	
16 SUPPLEMENTARY NOTATION					
17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	ESR EPR electron spin resonance)		
			Electron paramagnetic resonance)		
			In film phthalocyanine (Mg))		
19 ABSTRACT (Continue on reverse if necessary and identify by block number)					
<p>A computer program, written in FORTRAN, was developed to simulate ESR spectra of transition metal ions in thin layer phthalocyanine films. The spectral calculation is based on Gaussian distribution of orientations of the molecules plane of the phthalocyanine with respect to the surface of the film. Four ^{63}Cu hyperfine interactions are included to simulate the coordination site of the transition metal ion.</p>					
20 DISTRIBUTION AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21 ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED		
22a NAME OF RESPONSIBLE INDIVIDUAL M.D. Pace			22b TELEPHONE (Include Area Code) 22c OFFICE SYMBOL (202) 767-3239 Code 6120		

DD Form 1473, JUN 86

Previous editions are obsolete

S/N 0102-LF-01--0003

SECURITY CLASSIFICATION OF THIS PAGE

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A-1

FILMCAL
AN ESR SIMULATION PROGRAM FOR TRANSITION METALS IN
PHthalOCYANINE FILMS

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I. INTRODUCTION

The applications of ESR simulations of transition metal ions in phthalocyanines and porphyrins include oxygen transport in hemoglobin, and semiconducting films for microelectronic devices. One application is to understand chemiresistor gas sensors which are quartz substrates 5mm by 8mm with 40 interdigital gold fingers coated with Langmuir-Blodgett films of a semiconducting phthalocyanine (See figure 1.)

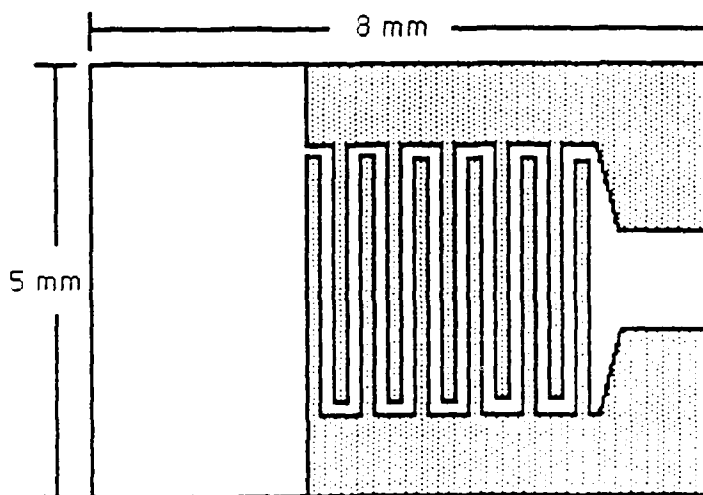


Figure 1
Schematic diagram of a chemiresistor with forty
interdigital gold electrodes coated with a Langmuir-
Blodgett film.

These devices have intrinsic conductivities which change when gaseous vapors are absorbed into the surface. Each gas gives a distinct change of conductivity for a given film. With an array of such detectors placed aboard a ship, one could monitor the levels of toxic gases present.

Unfortunately, the reaction time of the films is from 5 to 25 minutes with forty-five layers of phthalocyanine. In order for a film to recover its initial conductivity hours are needed. One factor which has a bearing on the time of recovery is how well ordered the phthalocyanine coating is on the device. The method used to transfer a layer of phthalocyanine onto the device is the Langmuir-Blodgett technique. This method transfers a layer from a water surface onto the substrate (See figure 2.)

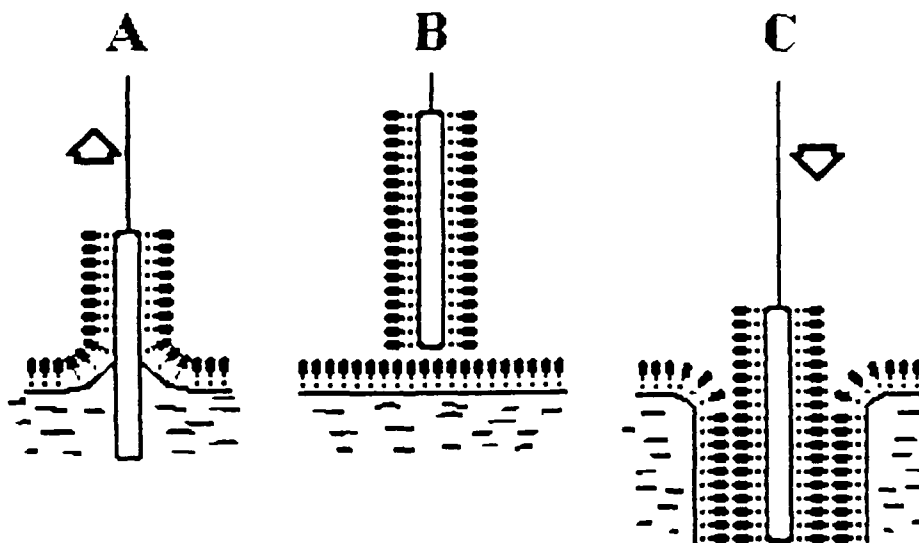


Figure 2

A transference of the phthalocyanine coating from the water surface to a substrate. The !s represent polarized molecules.

This method has its drawbacks since getting the coating to be perfectly ordered is difficult. This is due to changes in the surface tension of the water which must be monitored at all times to insure that the polarized coating is not disturbed. This computer program is helpful, for it allows the user to check how well ordered the film coating is once it is on the chemiresistor. This is due to the fact that an ordered film's spectrum will be completely different from that of an unordered film. The program allows the user to check possible molecular order parameters by means of spectral comparison between the simulated spectra and the experimental spectra.

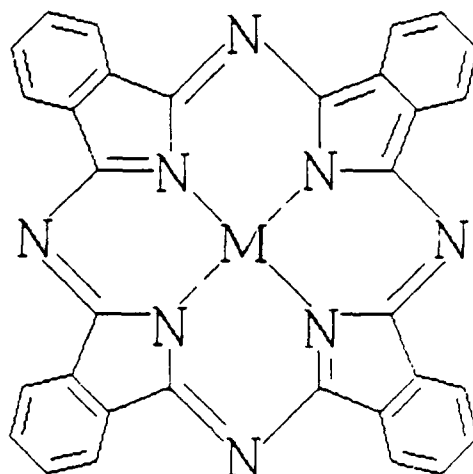


Figure 3

A metal-substituted phthalocyanine, where the M represents a metal atom and N a nitrogen.

Another application is with porphyrins which serve as structures of hemoglobin, chlorophyll, and some enzymes. Hemoglobins within the bloodstream complex with oxygen bound along the Z-axis and the porphyrin in the XY plane. When oxygen is unbound the iron is in the Fe^{3+} state having five d electrons with the electrons unpaired. This gives a paramagnetic molecule which is detected using ESR. Accurate simulation of the spectrum and comparison to the experimental spectrum can be used to determine the quantity of oxygen within the measured blood sample. So it is clear that this program has many practical uses.

II. THEORY

The program was written to calculate spectra for semiordered systems having $S=1/2$, or in the case of $S=1$ calculating the lines but not the intensities (The $S=1$ case does not formally calculate the lineshapes but it does calculate the magnetic fields at which the transitions occur for a completely random spectrum. Future versions of the program will include the lineshape). For the $S=1/2$ case the following spin Hamiltonian is used.

$$H = g\beta H \cdot S + S \cdot A^M \cdot I^M + S \cdot A^N \cdot I^N$$

where $S=1/2$; M denotes different metal ions having different hyperfine values (A) and different nuclear spin

numbers $I=1/2, 3/2, 5/2, \text{ or } 7/2$ and A^N denotes the superhyperfine coupling to the nitrogen ligands having $I^N=1$. N has values of 1 to 4 denoting the four near-neighbor nitrogen ligands. The nuclear Zeeman interaction and the ^{14}N quadrupole interaction are not included. These values are relatively small and in most cases do not affect the spectral lineshapes.

The program begins by setting up the parameters for the spectral calculations. The first question prompts the user to choose between several options available, the first being whether or not to include the spin=1 case. This $S=1$ case is used for situations where dimerization of the molecules results in spin pairing so that each paramagnetic species has $S=1$. The spectrum produced is derived by solving the following matrix for the value of D and E .

$$\begin{vmatrix} (D/3) + g\beta H_n & \frac{g\beta H(1-im)}{\sqrt{2}} & E \\ \frac{g\beta H(1+im)}{\sqrt{2}} & -2D/3 & \frac{g\beta H(1-im)}{\sqrt{2}} \\ E & \frac{g\beta H(1+im)}{\sqrt{2}} & (D/3) - g\beta H_n \end{vmatrix}$$

To formally calculate the transition probabilities a polynomial equation is solved for the field values at which pairs of energy levels are separated by $g H$. These fields are inserted into the above matrix which must be diagonalized to obtain the state energies and vectors. The transition intensities are computed from these equations. This must be carried out for each value of magnetic field orientation. This is time consuming and for this program the explicit calculation of the transition intensities has been omitted. Instead, we have programmed the general solution of the field values of the transitions when D and E are input. This can be used to aid in assignment of a completely random $S=1$ system when the experimental spectrum is available.

The case most often used is $S=1/2$. Within a normal phthalocyanine the metal atom in the center is the site of unpaired electron density. For $S=1/2$ this results in a hyperfine interaction between the nucleus of the metal and the unpaired electron spin. Depending on the bonding and electronegativities of the nitrogens the unpaired spin density can be delocalized sufficiently so that there is an interaction with the four surrounding nitrogen nuclei. These four nitrogen interactions add eight extra lines to the spectrum and must be accounted for in the lineshape procedure.

The choice of including second-order perturbation is the next option. When there is a large hyperfine interaction as with the transition metal ions the lines of the spectrum will be shifted

slightly from their first-order positions. To first order the distances between the transitions are equal. However, in the case of second order the transitions are shifted causing the lines to become unevenly spaced. This effect is shown in figure 4. Without the second order, metals like vanadyl, which has a nuclear spin moment of $7/2$ have computed spectra which are incorrect.

After making these selections, the user is requested to enter the number of nuclear spin isotopes. Then, for each isotope, the nuclear moment and % abundance is needed. When there is only one isotope, any constant is acceptable for the natural abundance.

The sweep width which is the range of points displayed on the X-axis is then needed. This entry is in gauss. The program will function with any sweep width size although it begins to lose accuracy if it is not in the range of 100 to 10000. The linewidth, the next piece of data, is the distance from peak-to-peak (in gauss) of a line.

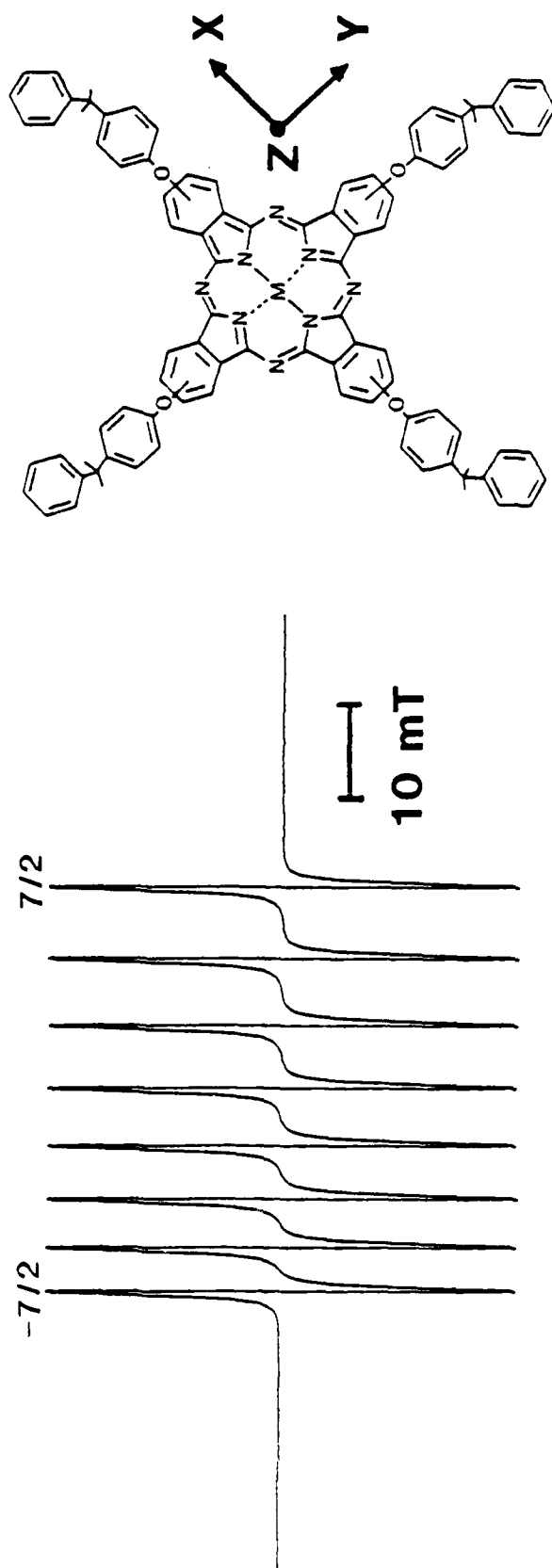
The next data is the g_x , g_y , and g_z grouping. These values are used for the calculation of the location of the hyperfine lines and are generally near the value of 2. The lower this value, the larger the gauss index; in other words, the spectrum is shifted farther to the right. The A_x , A_y , and A_z values are next input in gauss. These are the principal values of the hyperfine interaction tensor.

Then, the ^{14}N option is selected and the superhyperfine couplings are input. These are referred to as A_x , A_y , and A_z and have the same meaning as described above.

Once these data have been entered the program asks for angle rotations. This permits calculations of different orientations of the molecule within 3-D space. This space is referenced by the X, Y, and Z axes, with the angles of tilt from each being θ , ϕ , and ρ , respectively.

These choices are important because a spectrum of an ordered sample will look different depending on the angle at which you scan when using the ESR instrument. If a powder spectrum is being computed, the program should be allowed to scan all possible angle combinations. The reason is that the polymer sample is disordered and all orientations of the polymer molecules must be accounted for. The spectra are then averaged together to achieve the final result.

For Langmuir-Blodgett films, the coating is very layered and ordered, and this must be accounted for when computing the spectrum. The only problem with this is that the molecules usually align themselves not completely perpendicular or parallel to the surface, but rather at a bit of an angle. Sigma is the standard deviation of the most probable tilt angle. The option of entering the most probable angle allows the user to account for



m_I	$-7/2$	$-5/2$	$-3/2$	$-1/2$	$1/2$	$3/2$	$5/2$	$7/2$
ΔH (mT)	-21.8	-17.3	-12.2	-6.7	-0.7	5.7	12.7	20.1

FIGURE 4
Shifts of Spectral Lines Relative to the Center of the Spectrum
10 Gauss = 1 mT

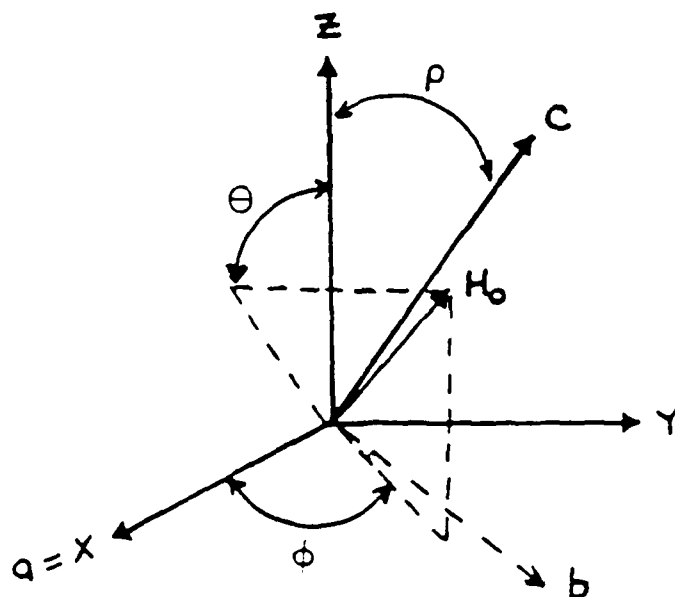
this. If the angle is unknown test spectra can be computed and compared to the experimental spectra recorded at different orientations of the film with respect to the applied magnetic field direction. By matching the experimental and computed spectra at all orientations, an assignment of the most probable tilt angle and standard deviation can be made. This assumes that one has accurately kept account of the coordinate axes of the experimental reference frame.

After programming these options, the program requires input for graphing. We decided to use the DISSPLA graphics package that was on the system. This graphing package uses calls to a calcomp plotter to do the plotting.

III. EXAMPLES OF SIMULATIONS

FILMCAL is an ESR (electron spin resonance) spectral simulation program for calculating semiordered systems having $S=1/2$ and $I=1/2, 3/2, 5/2$, or $7/2$. The program is specifically written to calculate transition metal ion ESR spectra of phthalocyanines and porphyrins which have a central metal ion coordinated to four near-neighbor ^{14}N atoms of the molecular rings. The hallmark of this program is the flexibility to calculate different orientational distributions of the molecular rings (phthalocyanines and porphyrins are planar ring-like molecules) with respect to a fixed XYZ frame of reference representing a substrate surface. The program has been extensively used to simulate ESR spectra of thin organometallic films composed of metal-substituted phthalocyanines; thereby determining the molecular packing arrangement of the molecules which comprise these films. This gives a direct and simple procedure for monitoring the molecular order of thin films by using the ESR spectra.

The program requires minimal input. An XYZ frame of reference is assigned as the substrate coordinate system with X normal to the substrate surface which is taken as the XY plane. A second coordinate system abc is assigned as the molecular axis system of the phthalocyanine molecule with c normal to the molecular plane which is the ab plane. This is shown schematically in figure 5. An angle ρ (ρ), defined as the tilt angle, is the angle between the Z axis of the substrate frame and the c axis of the molecular frame assuming that the X and a axes always lie coincident along the same direction. Only rotation about the X and a axes direction is allowed. This provides a means of specifying different tilt angles of the molecular plane (ab) with respect to the substrate plane (XY). Direction cosines are used to specify the direction of the polarizing magnetic field (H_0) with respect to the XYZ reference frame. Polar coordinates are used where θ (θ) is the angle between a component vector of H_0 in the ZX plane and the Z axis. ϕ (ϕ) is the angle of a component vector of H_0 in the XY plane from the X axis. This permits H_0 to be specified in any



abc molecular axes
and
XYZ reference axes

FIGURE 5.

direction and is analogous to an experiment where the substrate is rotated with respect to H_0 .

This gives sufficient degrees of freedom to specify any orientation of the molecular reference system with respect to XYZ and H_0 . For example, to calculate a spectrum corresponding to the molecular system coincident with the substrate system and with H_0 normal to the substrate plane (ie. along Z) we input:

A. EXAMPLE OF A POLYCRYSTALLINE SPECTRUM OF VO^{2+}
(SEE SPECTRUM FIG. 6)

Is this an S=1 case? 0 [where 1=yes and 0=no]

Include N-14 interaction? 0

Include 2nd order? 1

Number of isotopes? 1

Spin 1, nuclear moment=1.0 [when only one isotope any constant
is acceptable]

Spin number =3.5 [VO^{2+} nuclear spin of 7/2]

% abundance= 100.

Sweep width= 2000.

Linewidth= 10.0

$G_x = 1.9951$

$G_y = 1.9951$

$G_z = 1.9673$

Metal ion HFC values

$A_x = 59.7$ [input is in gauss]

$A_y = 59.7$

$A_z = 170.1$

----- Theta -----

Start = 0

Stop = 90

Step = 2

Pentaaquo Vanadyl(IV) ion in Frozen Aqueous Solution

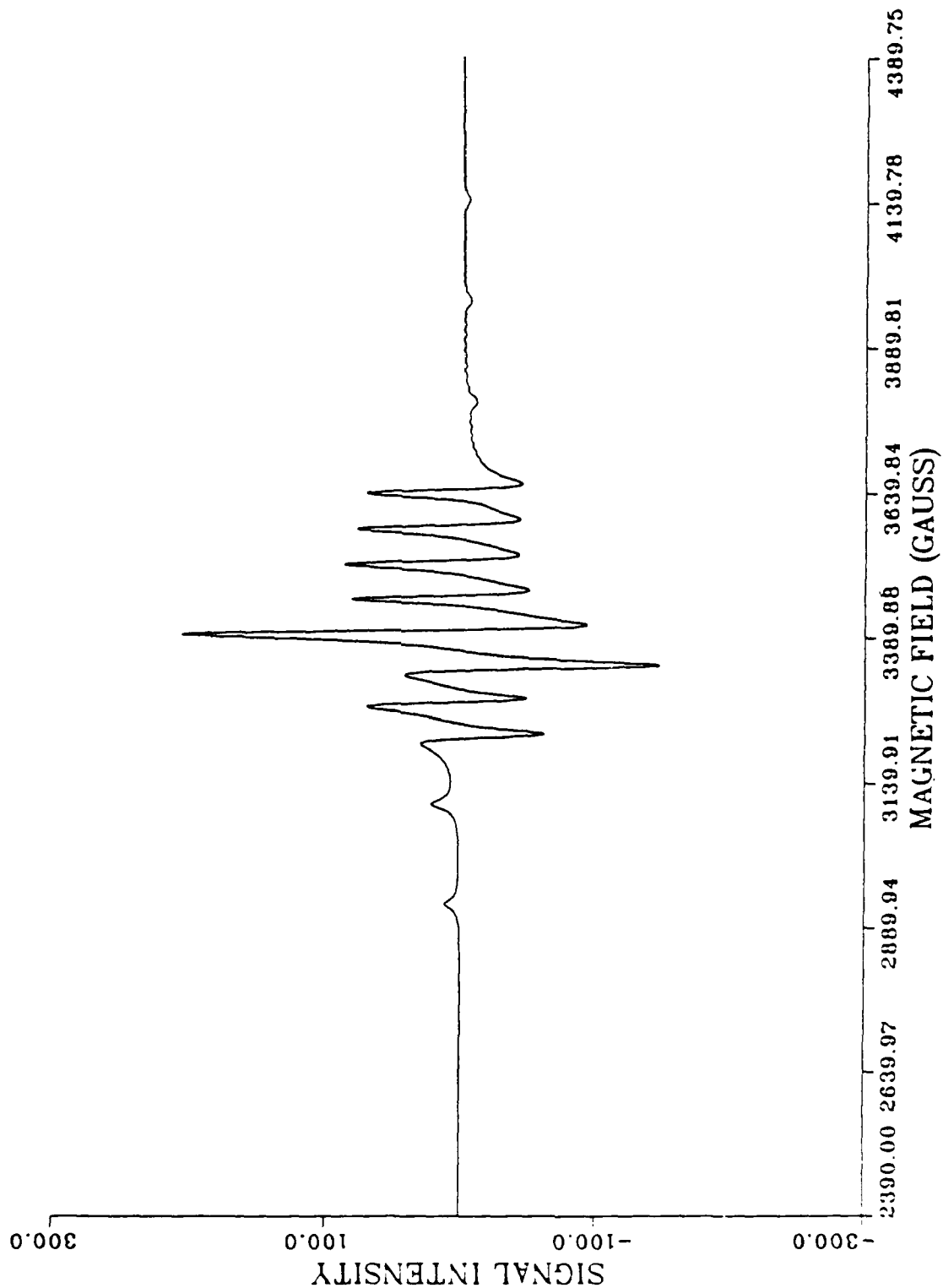


Figure 6.

Calibration = 1 [Calibration allows for steps between integer angles. For example an input might be:

Start=0
Stop = 1000
Step = 2
Calibration = 0.09

This would step from 0 to 90 degrees
by 500 steps ie. $1000 \times 0.09 = 90.$]

----- Phi -----

Pstart = 0

Pstop = 90

Pstep = 2

Calibration =1

----- Angle of Tilt From Z Axis -----

Start = 0

Stop = 90

Step = 2

Calibration = 1

----- Most Probable Angle of Tilt -----

Tilt angle = 0 [If Sigma is larger than 100 any value of the most probable tilt angle is okay. This will weight all tilt angles equally]

Sigma = 1000

Diluted Copper Phthalocyanine at Room Temperature

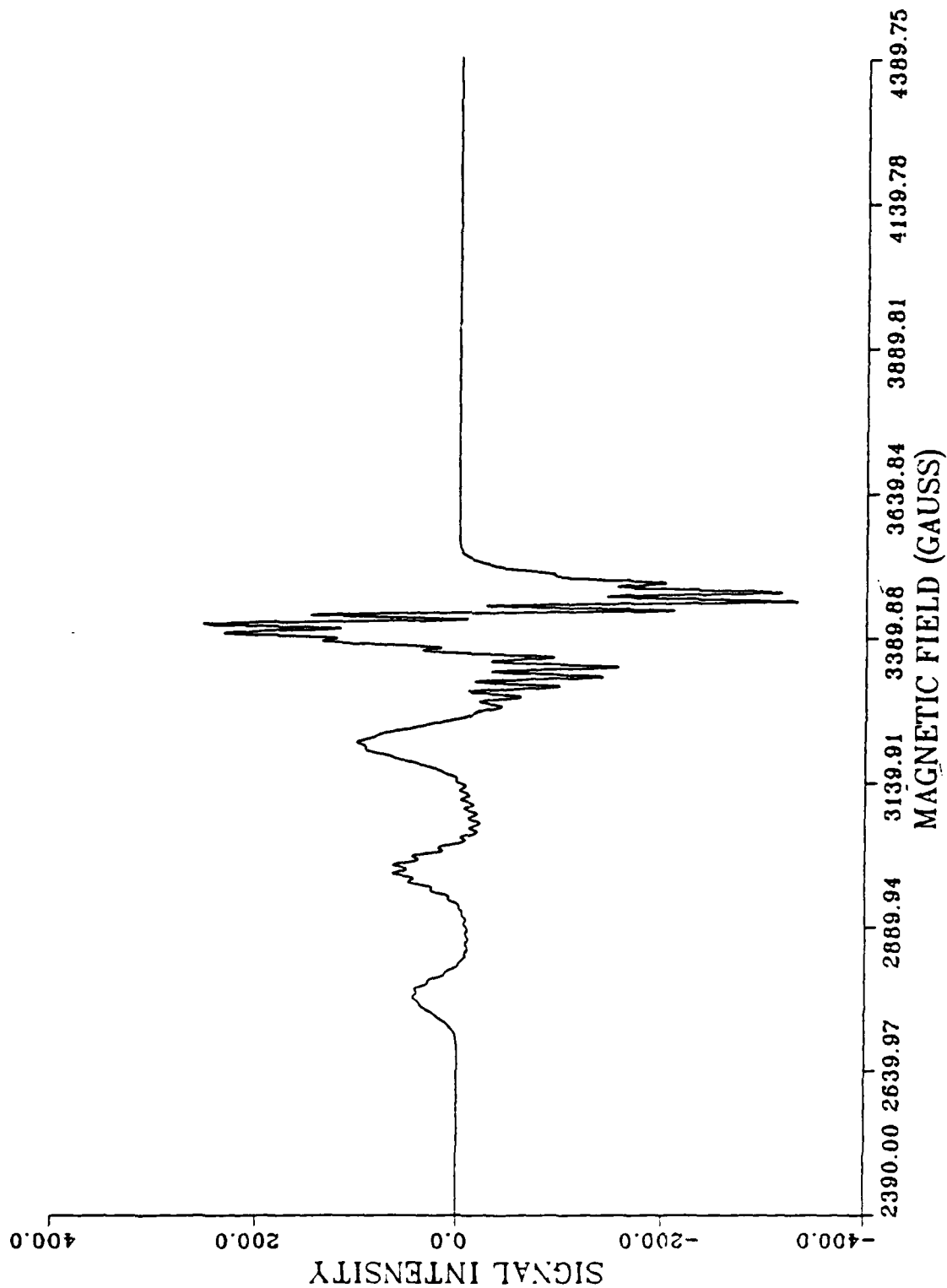


Figure 7.

B. EXAMPLE OF A POLYCRYSTALLINE SPECTRUM OF Cu^{2+}
(SEE SPECTRUM FIG. 7)

This example computes a polycrystalline ESR spectrum of copper phthalocyanine.

Is this a $S=1$ case? 0

Include N-14? 1

Include 2nd order? 0

Number of isotopes? 2

Spin 1, nuclear moment = 1.588

Spin number = 1.5

% abundance = 69.2

Sweep width = 2000.

Linewidth = 20.

$G_x = 2.045$

$G_y = 2.045$

$G_z = 2.187$

Metal ion HFC values

$A_x = 35.0$

$A_y = 35.0$

$A_z = 228.3$

N-14 SHFC values

$A_x = 17.1$

$A_y = 17.1$

$A_z = 15.5$

----- Theta -----

Start = 0

Stop = 90

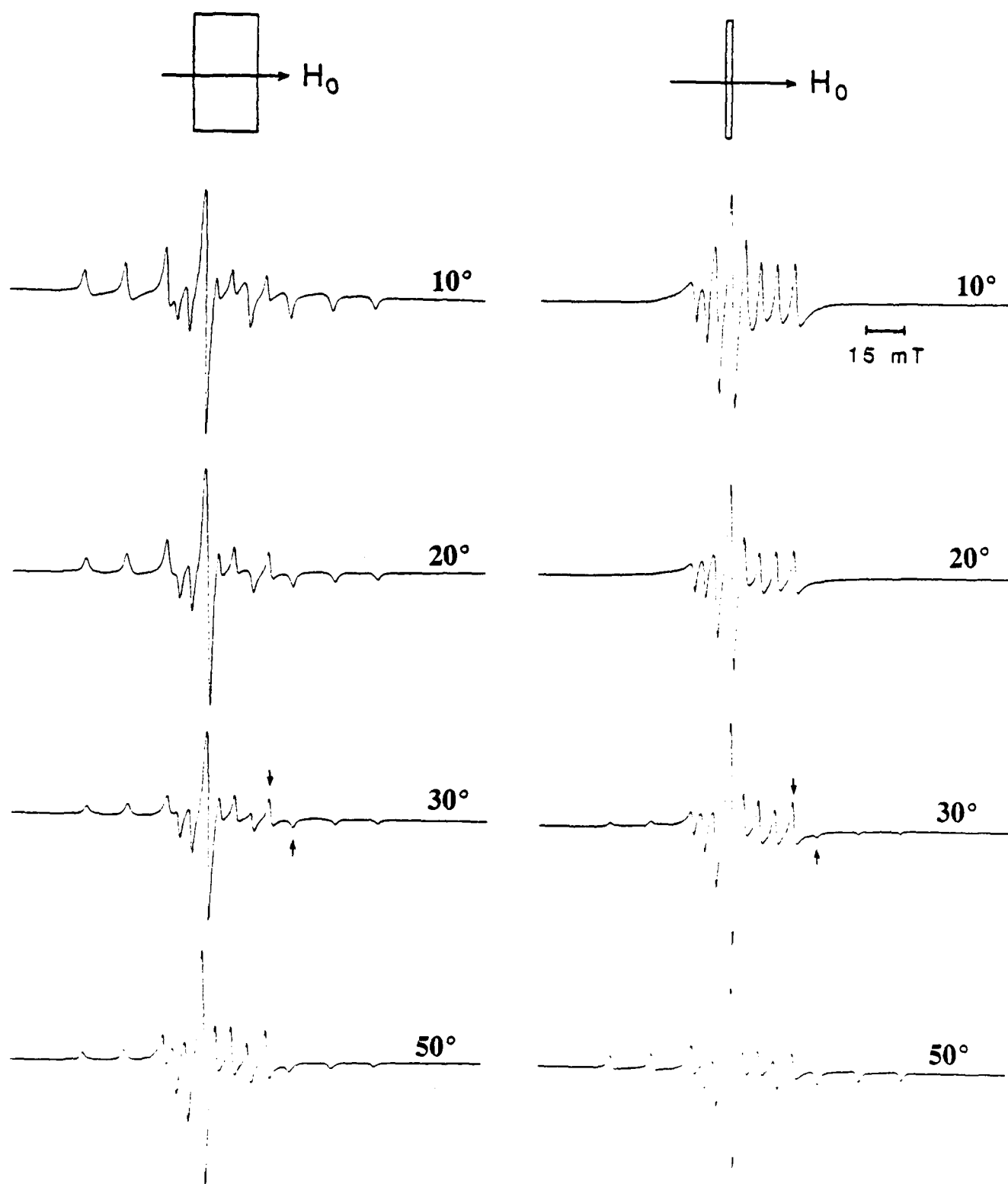


FIGURE 8.

Step = 2

Calibration = 1

----- Phi -----

Start = 0

Stop = 90

Step = 2

Calibration = 1

---- Angle of Tilt from Z Axis -----

Start = 0

Stop = 90

Step = 2

Calibration = 1

----- Most Probable Angle of Tilt -----

Tilt angle = 0

Sigma = 1000.

C. EXAMPLE OF LANGMUIR-BLODGETT FILM SPECTRA (SEE SPECTRA FIG. 8)

Disordered ESR spectra of an LB film of VOPCX₄ were calculated for two alignments of H₀ (parallel and perpendicular to the surface of the film). For these calculations the most probable tilt angle (ρ) is held constant at 80°. The tilt angle refers to the angle between the plane of the phthalocyanine ring and the planar surface of the substrate. The standard deviation is varied to simulate the disorder. The numbers 10°, 20°, 30°, 50° refer to the number of degrees of deviation of tilt angle from the value ρ . The disorder increases reading down each column.

IV. Listing of ESR spectral simulation program

PROGRAM FILMCAL

Filmcal - An ESR Simulation Program
Developed by Dale Pace & Stephanie Masumura
Naval Research Laboratory, July 1988

Filmcal is an ESR simulation program which calculates spectra of transition metal ions having $S=1/2$ and $I=1/2, 3/2, 5/2$, or $7/2$. The program was developed in order to simulate ESR spectra of organometallic films in which transition metal ions act as spin probes. The program operates by summing spectra of different values of theta (the angle between the polarizing magnetic field and the z principal axis of the g- and hfc tensors in the zx plane) and phi (the angle between H_0 and the x principal axis in the xy plane) and rho (the tilt angle of the g- and hfc tensors from the xyz reference frame). A tilt angle of the g-value and hfc tensors from the xyz principal axis reference frame is specified by the angle rho in order to simulate different orientations of molecules which make up the film. A weighting factor, W, is specified as a gaussian function in order to give different distributions of the molecular orientations within the film.

An approximate simulation of $S=1$ spectra is included as an option. This simulation calculates field positions of spectra having different D and E values to assist with $S=1$ assignments. The formal lineshapes and relative transition intensities are not included in this version of the program.

```
REAL LINE,LINE1,FLAG,TERM1,TERM2,MP,WINDOW
REAL G,HFC,THETA,H,SCALE,M7(8000),V(3,3,3),T(3,3,3)
REAL PLANCK,FREQ,PSI,RHO,CAL,PCAL,TCAL,W,SIGMA
REAL SRHO,CRHO,SSRHO,SCRHO,SPSI,CPSI,SSPSI,SCPSI
REAL AB(3),MO(3),SPIN(3),NWF(9),MRATIO,M(8)
REAL XARAY(8000),HIGHNUM,LOWNUM,LW,HR,XINCRE
REAL DEN,NUM,RANGE,INCRE,M8(8000),HZ,NUMBER,HX(8)
INTEGER LINE2,START,STOP,STEP,PSTEP,PSTART,PSTOP,TSTEP
INTEGER RHO1,RHO2,I,JJ,LTOTAL,N,SPAN
```

```
CONV=9.3377E-5
PLANCK=6.6252E-27
FREQ=9.5E9
BETA=0.92731E-20
GE=2.0023
```

-----INITIALIZATIONS-----

```
DO 10 I=1,3
DO 11 J=1,3
DO 12 K=1,3
```

```

      V(I,J,K)=0
12  CONTINUE
11  CONTINUE
10  CONTINUE
    DO 44 I=1,8000
      M7(I)=0
      M8(I)=0
      XARRAY(I)=I
44  CONTINUE
    PSI=0.0
C-----SET-UP-----
    PRINT *, 'SET-UP'
    PRINT *, 'YES=1      NO=0'
    PRINT '(A,$)', ' IS THIS A S=1 CASE? '
    ACCEPT *, FS
    IF (FS.EQ.1) THEN
      PRINT '(A,$)', ' D= '
      ACCEPT *, D
      PRINT '(A,$)', ' E= '
      ACCEPT *, E
      PRINT '(A,$)', ' SWEEPWIDTH= '
      ACCEPT *, SW
      PRINT '(A,$)', ' LINEWIDTH= '
      ACCEPT *, LW
      WINDOW=3390-(SW/2)
      GOTO 9999
    ENDIF
    PRINT '(A,$)', ' INCLUDE N-14 INTERACTION? '
    ACCEPT *, F1
    PRINT '(A,$)', ' INCLUDE 2ND ORDER? '
    ACCEPT *, F2
C-----ISOTOPE/GRAPHING DATA-----
    PRINT '(A,$)', ' NUMBER OF NUCLEAR SPIN ISOTOPES? '
    ACCEPT *, N
    DO 13 I=1,N
      PRINT 2,I
      2  FORMAT(' SPIN',I3,' NUCLEAR MOMENT= ', $)
      ACCEPT *, MO(I)
      PRINT '(A,$)', ' SPIN NUMBER=(DECIMAL) '
      ACCEPT *, SPIN(I)
      PRINT '(A,$)', ' % ABUNDANCE= '
      ACCEPT *, AB(I)
13  CONTINUE
    PRINT '(A,$)', ' SWEEP WIDTH= '
    ACCEPT *, SW
    SCALE=NINT(8000/SW)
    WINDOW=3390-(SW/2)
    PRINT '(A,$)', ' LINEWIDTH= '
    ACCEPT *, LW
C-----DATA VALUES-----
9999 PRINT '(A,$)', ' GX= '
      ACCEPT *, V(1,1,1)
      PRINT '(A,$)', ' GY= '
      ACCEPT *, V(2,2,1)

```

```

      PRINT '(A,$)', ' GZ= '
      ACCEPT *, V(3,3,1)
      IF (FS.EQ.1) GOTO 9998
C-----HFC DATA-----
      PRINT *, 'METAL ION HFC VALUES'
      PRINT '(A,$)', ' AX= '
      ACCEPT *, V(1,1,2)
      PRINT '(A,$)', ' AY= '
      ACCEPT *, V(2,2,2)
      PRINT '(A,$)', ' AZ= '
      ACCEPT *, V(3,3,2)
C-----N-14 DATA-----
      IF (F1.EQ.1) THEN
      PRINT *, 'N-14 SHFC VALUES'
      PRINT '(A,$)', ' AX= '
      ACCEPT *, V(1,1,3)
      PRINT '(A,$)', ' AY= '
      ACCEPT *, V(2,2,3)
      PRINT '(A,$)', ' AZ= '
      ACCEPT *, V(3,3,3)
      NWF(1)=1
      NWF(2)=4
      NWF(3)=10
      NWF(4)=16
      NWF(5)=19
      NWF(6)=16
      NWF(7)=10
      NWF(8)=4
      NWF(9)=1
      ENDIF
C-----
      DO 25 K=1,3
      DO 26 I=1,3
      DO 27 J=1,3
        V(I,J,K) = V(I,J,K) * V(I,J,K)
        PRINT 1,I,J,K,V(I,J,K)
1      FORMAT (' V(',I2,',',I2,',',I2,')=',G16.8)
27      CONTINUE
26      CONTINUE
25      CONTINUE
C-----ANGLES-----
      PRINT *, '----- THETA -----'
      PRINT '(A,$)', ' START= '
      ACCEPT *, START
      PRINT '(A,$)', ' STOP= '
      ACCEPT *, STOP
      PRINT '(A,$)', ' STEP= '
      ACCEPT *, STEP
      PRINT '(A,$)', ' CALIBRATION= '
      ACCEPT *, CAL
      PRINT *, '----- PHI -----'
      PRINT '(A,$)', ' PSTART= '
      ACCEPT *, PSTART
      PRINT '(A,$)', ' PSTOP= '

```

```

ACCEPT *,PSTOP
PRINT '(A,$)',PSTEP= '
ACCEPT *,PSTEP
PRINT '(A,$)',CALIBRATION= '
ACCEPT *,PCAL
PRINT *,'-----'
PRINT *,'ANGLE OF TILT FROM Z-AXIS'
PRINT '(A,$)',START= '
ACCEPT *,RHO1
PRINT '(A,$)',STOP= '
ACCEPT *,RHO2
PRINT '(A,$)',STEP= '
ACCEPT *,TSTEP
PRINT '(A,$)',CALIBRATION= '
ACCEPT *,TCAL
PRINT *,'-----'
PRINT *,'MOST PROBABLE TILT'
PRINT '(A,$)',TILT ANGLE= '
ACCEPT *,MP
MP = MP * .01745
PRINT '(A,$)',SIGMA= '
ACCEPT *,SIGMA
SIGMA=SIGMA*SIGMA
DO 1000 I=START,STOP,STEP
THETA = .01745 * I * CAL
DO 2000 J=PSTART,PSTOP,PSTEP
PHI = .01745 * J * PCAL
X=SIN(THETA)*COS(PHI)
Y=SIN(THETA)*SIN(PHI)
Z=COS(THETA)
DO 50 II=RHO1,RHO2,TSTEP
RHO = -.01745 * II * TCAL
W=(MP+RHO)/.01745
W=EXP(-(W * W) / (2 * SIGMA))
C-----CALCULATIONS WITHOUT THE SECOND ORDER-----
IF (F2.EQ.0) THEN
  SRHO=SIN(RHO)
  CRHO=COS(RHO)
  SSRHO=SIN(RHO)*SIN(RHO)
  SCRHO=COS(RHO)*COS(RHO)
  SPSI=SIN(PSI)
  CPSI=COS(PSI)
  SSPSI=SIN(PSI)*SIN(PSI)
  SCPSI=COS(PSI)*COS(PSI)
  DO 70 K=1,3
C-----INTERMEDIATE CALCULATIONS FOR G AND HFC
  T(1,1,K)=(V(1,1,K)*SCPSI)+((SSPSI)*((V(2,2,K)*SSRHO
1    +(V(3,3,K)*SCRHO))))
  T(1,2,K)=SPSI*((V(2,2,K)*SRHO*CRHO)-(V(3,3,K)*SRHO*CRHO))
  T(1,3,K)=(-V(1,1,K)*CPSI*SPSI)+(CPSI*SPSI*((V(2,2,K)*SSRHO
1    +(V(3,3,K)*SCRHO)))
C
  T(2,1,K)=(SPSI*((V(2,2,K)*CRHO*SRHO-(V(3,3,K)
1    *SRHO*CRHO))))

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```

      T(2,2,K)=(V(2,2,K)*SCRHO)+(V(3,3,K)*SSRHO)
      T(2,3,K)=CPSI*((V(2,2,K)*CRHO*SRHO)-(V(3,3,K)*SRHO*CRHO))
C
      T(3,1,K)=((-V(1,1,K)*SPSI*CPSI)+(SPSI*CPSI
1      *((V(2,2,K)*SSRHO)+(V(3,3,K)*SCRHO))))
      T(3,2,K)=CPSI*((V(2,2,K)*SRHO*CRHO)-(V(3,3,K)*SRHO*CRHO))
      T(3,3,K)=(V(1,1,K)*SSPSI)+(CPSI*((V(2,2,K)*SSRHO
1      +(V(3,3,K)*SCRHO)))
70    CONTINUE
C-----CALCULATION OF G AND HFC WITH VALUES FROM ABOVE-----
      K=1
      G=SQRT(X*X*T(1,1,K) + X*Y*T(2,1,K) + X*Z*T(3,1,K)
1      + X*Y*T(1,2,K) + Y*Y*T(2,2,K) + Y*Z*T(3,2,K)
1      + X*Z*T(1,3,K) + Y*Z*T(2,3,K) + Z*Z*T(3,3,K))
C
      K=2
      HFC=SQRT(X*X*T(1,1,K) + X*Y*T(2,1,K) + X*Z*T(3,1,K)
1      + X*Y*T(1,2,K) + Y*Y*T(2,2,K) + Z*Y*T(3,2,K)
1      + X*Z*T(1,3,K) + Y*Z*T(2,3,K) + Z*Z*T(3,3,K))
C-----N-14 INTERACTION-----
      IF (F1.EQ.1) THEN
        K=3
        NHFC=SQRT(X*X*T(1,1,K)+X*Y*T(2,1,K)+X*Z*T(3,1,K)
1      +X*Y*T(1,2,K)+Y*Y*T(2,2,K)+Z*Y*T(3,2,K)
1      +Z*X*T(1,3,K)+Z*Y*T(2,3,K)+Z*Z*T(3,3,K))
        ENDIF
C-----
      H=PLANCK*FREQ/(G*BETA)
      DO 3000 III=1,N
        LTOTAL=2*SPIN(III)+1
        LTOTAL=LTOTAL-1
        MRATIO=MO(III)/MO(1)
        LLOW=(HFC*LTOTAL*MRATIO)/2
        DO 210 JJJ=0,LTOTAL
          TERM1=HFC*JJJ*MRATIO
          LINE=H-LLOW+TERM1
C-----N-14 INTERACTION PLACEMENT OF NITROGEN LINES-----
          IF (F1.EQ.1) THEN
            DO 211 KKK=1,9
              TERM2=NHFC*(KKK-5)
              LINE1=LINE+TERM2
              LINE2=NINT((LINE1-WINDOW)*SCALE)
              IF(LINE2.LE.8000.AND.LINE2.GT.0) M7(LINE2)=M7(LINE2)
1              +W*AB(III)*NWF(KKK)
211            CONTINUE
C-----PLACEMENT OF LINES/NON-NITROGEN-----
          ELSE
            LINE2=NINT((LINE-WINDOW)*SCALE)
            IF (LINE2.LE.8000) M7(LINE2)=M7(LINE2)+W*AB(III)
            ENDIF
C-----
210      CONTINUE
3000    CONTINUE
C-----SECOND ORDER CASE-----

```

```

ELSE
  CTHETA=SIN(THETA)*SIN(PHI)*SIN(RHO)+COS(THETA)*COS(RHO)
  STHETA=ABS(1-(CTHETA*CTHETA))
  STHETA=SQRT(STHETA)
  G=SQRT(V(3,3,1)*CTHETA*CTHETA+V(1,1,1)*STHETA*STHETA)
  HFC=(SQRT((V(3,3,2)*V(3,3,1)*CTHETA*CTHETA)
1   +(V(1,1,2)*V(1,1,1)*STHETA*STHETA)))
  HFC=HFC/G
C-----SECOND ORDER/N-14 INTERACTION-----
  IF(F1.EQ.1)THEN
    NHFC=SQRT((V(3,3,3)*V(3,3,1)*CTHETA*CTHETA)
1   +(V(1,1,3)*V(1,1,1)*STHETA*STHETA))
    ENDIF
C-----
  DO 60 III=1,N
    LTOTAL=2*SPIN(III)+1
    LTOTAL=LTOTAL-1
    MRATIO=MO(III)/MO(1)
    MI=-(SPIN(III))
    DO 61 JJJ=0,LTOTAL
      A=(V(1,1,2)*CONV*CONV*(V(3,3,2)*CONV*CONV
1     +HFC*HFC*CONV*CONV))
      A=A/(4*3.169*HFC*HFC*CONV*CONV)
      A=A*(15.75-(MI*MI))
      B=((V(1,1,2)*CONV*CONV-V(3,3,2)*CONV*CONV)/(HFC*CONV))
      B=B*B
      B=(.5*B)/.3169
      E=STHETA*STHETA*CTHETA*CTHETA
      B=B*E*MI*MI
      LINE=(0.3169+HFC*MI*CONV*MRATIO-A-B)/(G*4.6686E-5)
C-----SECOND ORDER/N-14 INTERACTION-----
C-----PLACEMENT OF NITROGEN LINES-----
      IF (F1.EQ.1) THEN
        DO 62 KKK=1,9
          TERM2=NHFC*(KKK-5)
          LINE1=LINE+TERM2
          LINE2=NINT((LINE1-WINDOW)*SCALE)
          IF(LINE2.LE.8000) M7(LINE2)=M7(LINE2)+W*AB(III)*NWF(KKK)
62      CONTINUE
C-----PLACEMENT OF LINES W/O N-14-----
      ELSE
        LINE2=NINT(ABS((LINE-WINDOW)*SCALE))
        IF (LINE2.LE.8000.AND.LINE2.GT.0) M7(LINE2)=M7(LINE2)+W*AB(III)
        ENDIF
C-----
      MI=MI+1
61      CONTINUE
60      CONTINUE
    ENDIF
C-----END OF SECOND ORDER-----
50      CONTINUE
2000     CONTINUE
1000     CONTINUE
      GO TO 3010

```



```

C-----S=1 CASE-----
9998 BETA2=4.6686E-5
HO=(PLANCK*FREQ)/(GE*BETA)
DP=D/(GE*BETA2)
EP=E/(GE*BETA2)
IF ((DP**2-(3*(EP**2))).GT.0) DPS=SQRT(DP**2-(3*(EP**2)))
SCALE=NINT(8000/SW)
HX(1)=(GE/V(3,3,1))**2*(((HO-DP)**2)-(EP*EP))
HX(2)=(GE/V(2,2,1))**2*((HO-DP-EP)*(HO-(EP**2)))
HX(3)=(GE/V(1,1,1))**2*((HO-DP+EP)*(HO+(EP**2)))
HX(4)=(GE/V(1,1,1))**2*((HO+DP-EP)*(HO-(EP**2)))
HX(5)=(GE/V(2,2,1))**2*((HO+DP+EP)*(HO+(EP**2)))
HX(6)=(GE/V(3,3,1))**2*((HO+DP)**2-(EP*EP))
HX(7)=((HO/2)**2-(DPS**2/3))
HX(8)=(HO**2-(DPS**2/3))
DO JJJ=1,8
  IF (HX(JJJ).GT.0.AND.HX(JJJ).NE.0) THEN
    HX(JJJ)=SQRT(HX(JJJ))
    SINDEXT=NINT(((HX(JJJ)-WINDOW)/((8000/SCALE)/8000))-1)
    IF(SINDEXT.GT.0.AND.SINDEXT.LT.(WINDOW+SW))
      1 M7(SINDEXT)=M7(SINDEXT)+1
  ENDIF
ENDDO
C-----LINE SHAPE DETERMINATION-----
3010 PRINT *, 'DETERMINING THE LINE SHAPE OF THE SPECTRUM'
SPAN=2*SCALE*LW
LW=(LW/SW)*8000
DO 4000 I=1,8000
  IF(M7(I).GT.0) THEN
    DO 5000 J=0,SPAN
      HZ=XARRAY(I+J)*SCALE
      HR=XARRAY(I)*SCALE
      NUM=2*LW*LW*(HZ-HR)
      DEN=LW*LW+((HZ-HR)*(HZ-HR))
      DEN=DEN*DEN
      IF (J+I.LE.8000) M8(I+J)=-M7(I)*(NUM/DEN)+M8(I+J)
      IF (J.GT.1) THEN
        IF (I-J.GT.0) M8(I-J)=M7(I)*(NUM/DEN)+M8(I-J)
      ENDIF
    5000 CONTINUE
  ENDIF
4000 CONTINUE
C-----DETERMINATION OF EXTREME Y VALUES-----
HIGHNUM=M8(1)
LOWNUM=M8(1)
DO 33 JJJ=2,8000
  IF (M8(JJJ).GT.HIGHNUM) THEN
    HIGHNUM=M8(JJJ)
  ELSE IF (M8(JJJ).LT.LOWNUM) THEN
    LOWNUM=M8(JJJ)
  ENDIF
33 CONTINUE
C-----SCALING UP OR DOWN OF VALUES-----
C-----TO CREATE A BETTER GRAPH-----

```

```

NUMBER=ABS(LOWNUM)
IF (HIGHNUM.GT.NUMBER) THEN
  NUMBER=HIGHNUM
ENDIF
IF (NUMBER.LT.60.AND.NUMBER.NE.0) THEN
999  DO 36 KKK=1,8000
    M8(KKK)=M8(KKK)*10
36  CONTINUE
    NUMBER=NUMBER*10
    IF (NUMBER.LT.60) GOTO 999
    ELSE IF (NUMBER.GT.1000) THEN
199  DO 39 KKK=1,8000
    M8(KKK)=M8(KKK)/10
39  CONTINUE
    NUMBER=NUMBER/10
    IF (NUMBER.GT.1000) GOTO 199
ENDIF
C-----DETERMINATION OF A SUITABLE RANGE FOR GRAPHING-----
  RANGE=(INT(NUMBER/100)+1)*100*1.
C-----DETERMINATION OF A SUITABLE INCREMENT FOR Y-AXIS-----
  INCRE=100.
  NUM=RANGE/100
  IF (NUM MOD 2.EQ.0)THEN
    INCRE=200.
  ENDIF
C-----SCALES THE X ARRAY CORRECTLY INTO GAUSS-----
  RATE=((8000/SCALE)/8000)
  XARAY(1)=WINDOW
  DO 49 III=2,8000
    XARAY(III)=XARAY(III-1)+RATE
49  CONTINUE
  XINCRE=(XARAY(8000)-WINDOW)/8
C-----GRAPHING OF THE SPECTRA WITH DISSPLA 9.2-----
  PRINT *, 'PREPARING TO GRAPH THE SPECTRUM'
  CALL COMPRS
  CALL PAGE(11.,8.5)
  CALL TRIPLX
  CALL TITLE ('TITLES',100,'MAGNETIC FIELD (GAUSS)$',100,
1  'SIGNAL INTENSITY$',100,8.,5.5)
  CALL GRAF (WINDOW,XINCRE,XARAY(8000),-(RANGE),INCRE,RANGE)
  CALL CURVE(XARAY,M8,8000,0)
  CALL ENDPL(0)
  CALL DONEPL
END

```

v. Bibliography

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VI. DISKETTE

The source code FILMCAL.FOR compiles using MICROSOFT FORTRAN using the FL/Gt command. The field values of array XARAY(8000) and the intensities of array M8(8000) are output in SYS\$OUT. These arrays may be dimensioned to different lengths by changing the appropriate dimension statements and loop counters in the program. A plotting program such as ASYST must be used to plot the SYS\$OUT file and is not included in the program code.

An diskette of the program is available from:

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